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VG10-174

Optically-Based Diagnostics for Gas-Phase Laser Development

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XVIII International Symposium on Gas Flow and Chemical Lasers and High Power Lasers 2010
Sofia, Bulgaria

August 2010

Acknowledgement of Support and Disclaimer
This material is based upon work supported by Air Force Office of Scientific Research under Contract Number FA9550-07-1-0575. Any opinions, findings and conclusions or recommendations expressed in this material are those of the author(s) and do not necessarily reflect the views of Air Force Office of Scientific Research.

Report Documentation Page

Form Approved
OMB No. 0704-0188

1. REPORT DATE **AUG 2010**	2. REPORT TYPE	3. DATES COVERED **00-00-2010 to 00-00-2010**

4. TITLE AND SUBTITLE **Optically-Based Diagnostics for Gas-Phase Laser Development**	5a. CONTRACT NUMBER 5b. GRANT NUMBER 5c. PROGRAM ELEMENT NUMBER
6. AUTHOR(S)	5d. PROJECT NUMBER 5e. TASK NUMBER 5f. WORK UNIT NUMBER
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) **Physical Sciences Inc,20 New England Business Center,Andover,MA,01810**	8. PERFORMING ORGANIZATION REPORT NUMBER
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)	10. SPONSOR/MONITOR’S ACRONYM(S) 11. SPONSOR/MONITOR’S REPORT NUMBER(S)

12. DISTRIBUTION/AVAILABILITY STATEMENT
Approved for public release; distribution unlimited

13. SUPPLEMENTARY NOTES

14. ABSTRACT

15. SUBJECT TERMS

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT **unclassified**	b. ABSTRACT **unclassified**	c. THIS PAGE **unclassified**	**Same as Report (SAR)**	**28**	

Overview

- **Theme: multi-species diagnostics for absolute concentrations are essential for effective development of high-energy gas lasers**
  - Precursor production, loss, optimization
  - Transference from subscale reactors
  - Scaling of gain, power, efficiency

- **Current applications**
  - Electric Oxygen Iodine Laser (EOIL): precursor kinetics and gain dynamics
  - Related systems: COIL, micro-COIL
  - Alkali laser systems: DPAL, XPAL gain, multi-photon effects

- **Outline of presentation:**
  - Brief overview of diagnostics and apparatus
  - Absolute emission spectrometry
    - Near-infrared spectroscopy: $O_2(a^1\Delta_g)$, $I(^2P_{1/2})$
    - Air afterglow photometry: $O(^3P)$
  - Ultrasensitive absorption photometry: I_2, O_3
  - High-resolution absorption/gain spectroscopy: atomic iodine, alkali metals

Role of Optical Diagnostics in High Energy Gas Laser Development

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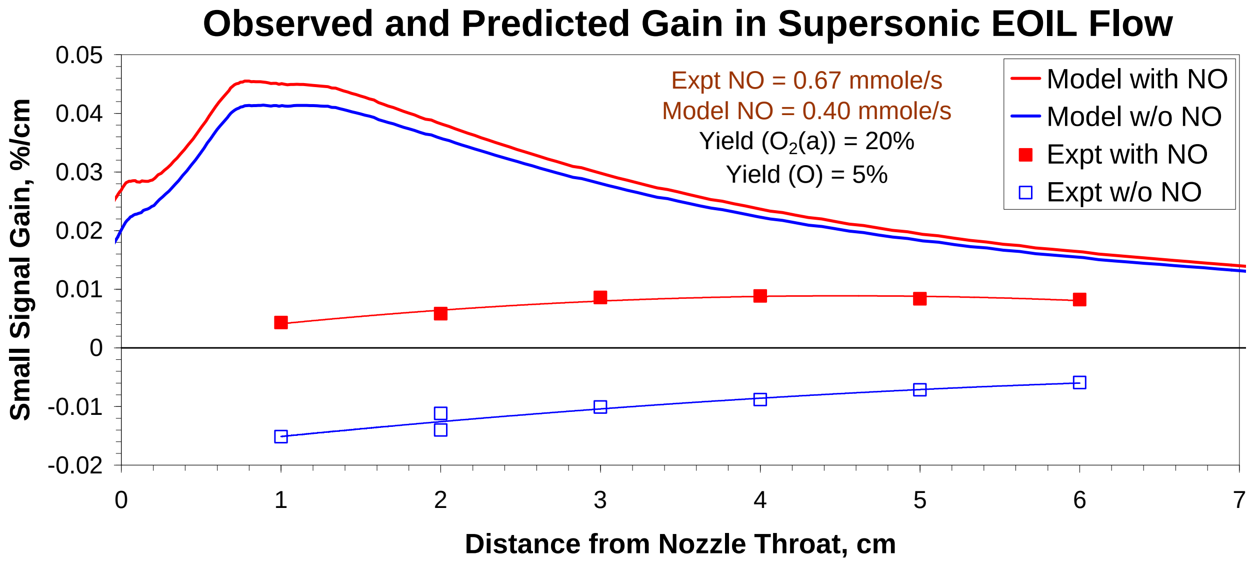
- **Chemically rich, energetic, reacting flow with competing phenomena**
  - Multispecies detection required
  - COIL, EOIL: O_2(a,b), I*, I, I_2, gain, T, O, O_3
  - DPAL, XPAL: ground-state M, numerous M*, M_2*, MX*, gain
- **Objective: detect key species concentrations vs. flow time**
  - Vary operating conditions systematically
  - Quantify species production and loss rates
  - Relate to system design requirements
- **Put a "cage" around the model:**



Electric Oxygen Iodine Laser (EOIL)

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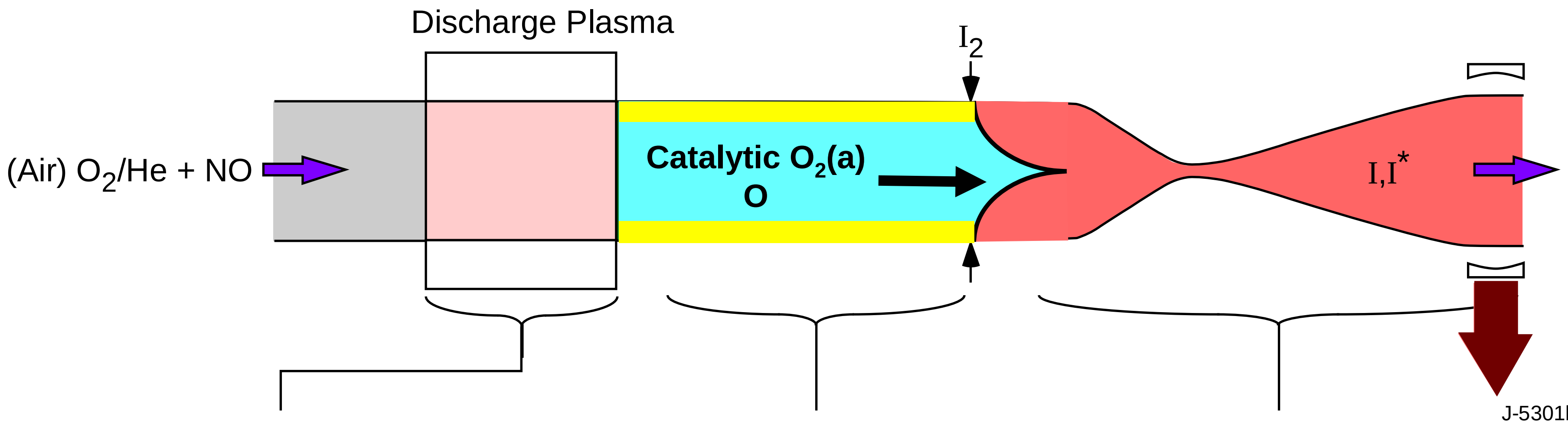

$e^- + O_2 \rightarrow O_2(a) + e^-$

$e^- + O_2 \rightarrow O + O + e^-$

Ionization

$e^- + O_2(a) \rightarrow \text{losses}$

Dilution in He required

$O + NO + M \rightarrow NO_2 + M$

$O + NO_2 \rightarrow NO + O_2$

$O + O_2 + M \rightarrow O_3 + M$

$O + O_3 \rightarrow O_2 + O_2$

$NO + O_3 \rightarrow O_2 + NO_2$

$O + I_2 \rightarrow IO + I$

$O + IO \rightarrow O_2 + I$

$\boxed{O_2(a) + I \rightleftarrows O_2 + I^*}$

$O + I^* \rightarrow O + I$

$I^* + O_2 \rightarrow I + O_2(v)$

$$\frac{[I^*]}{[I]} \rightarrow K_{EQ}(T)\frac{[O_2(a)]}{[O_2]}$$

Hybrid EOIL: Catalytically enhanced $O_2(a)$

PSI Microwave Discharge Flow Reactors
(2450 MHz)

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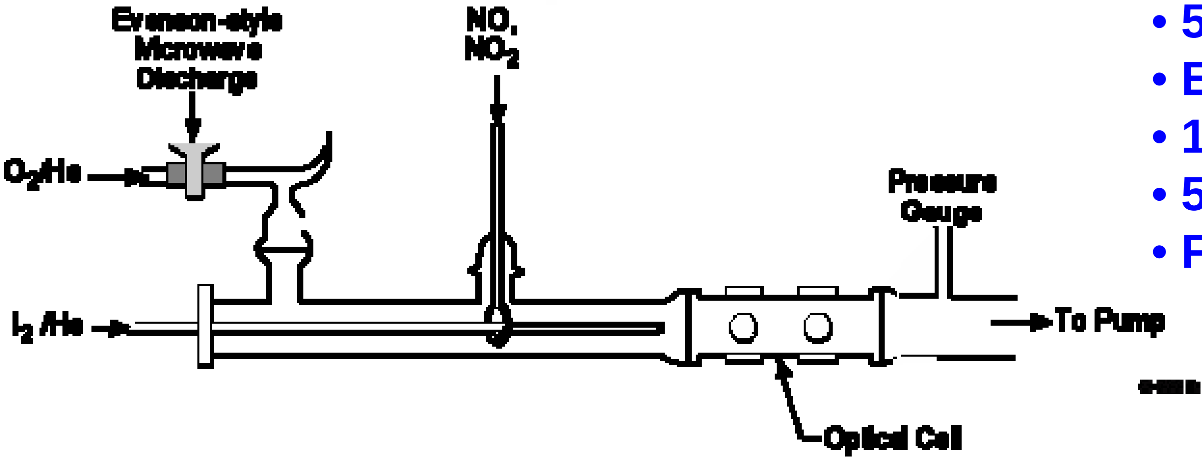
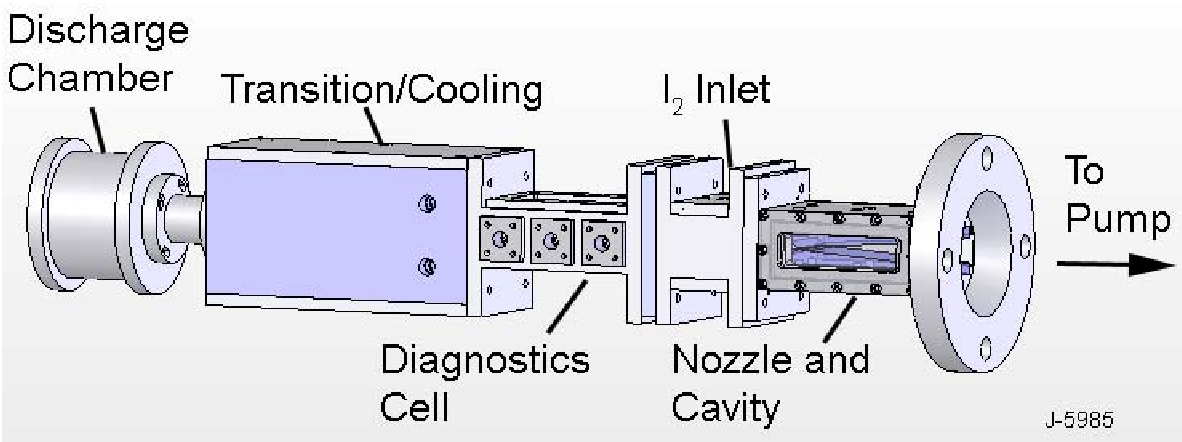
Low-Pressure Reactor: Active-O_2 Kinetics



- 50-100 W, 10-100 Td
- External cavity discharge
- 1-10 Torr, 1-5 mmole/s
- 5-cm i.d. Pyrex flow tube
- Flow T ~ 300-350 K

EOIL Subsonic/Supersonic Reactor

- 1-5 kW, 10-50 Td
- Coaxial MIDJet discharge
- 30-70 Torr, 40-100 mmole/s
- M ~ 2 supersonic cavity
- Lasing typically 100-150 mW
  -- $M^2 = 1.08 \pm 0.01$



Near-IR Absolute Emission: O_2(a) and I*

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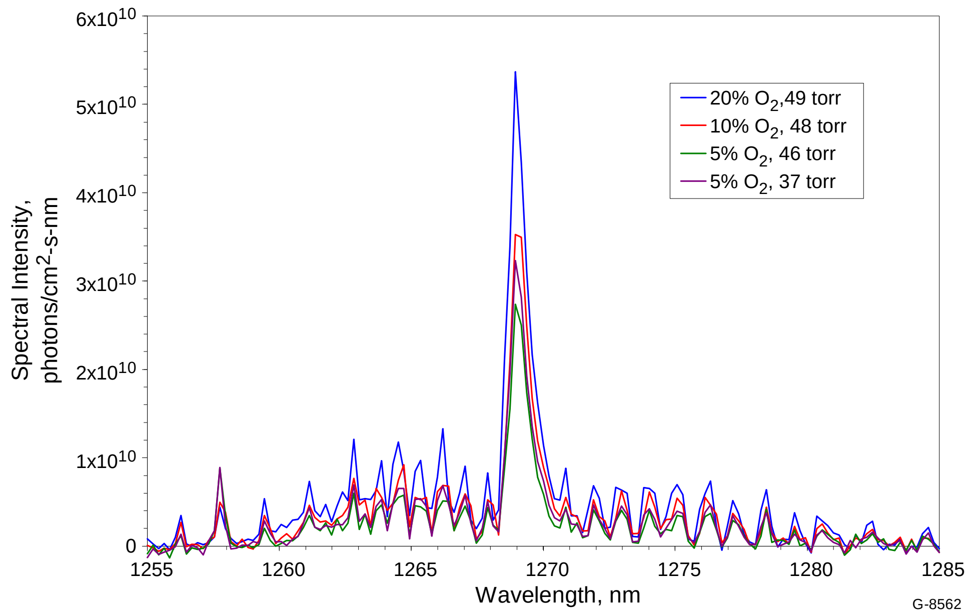
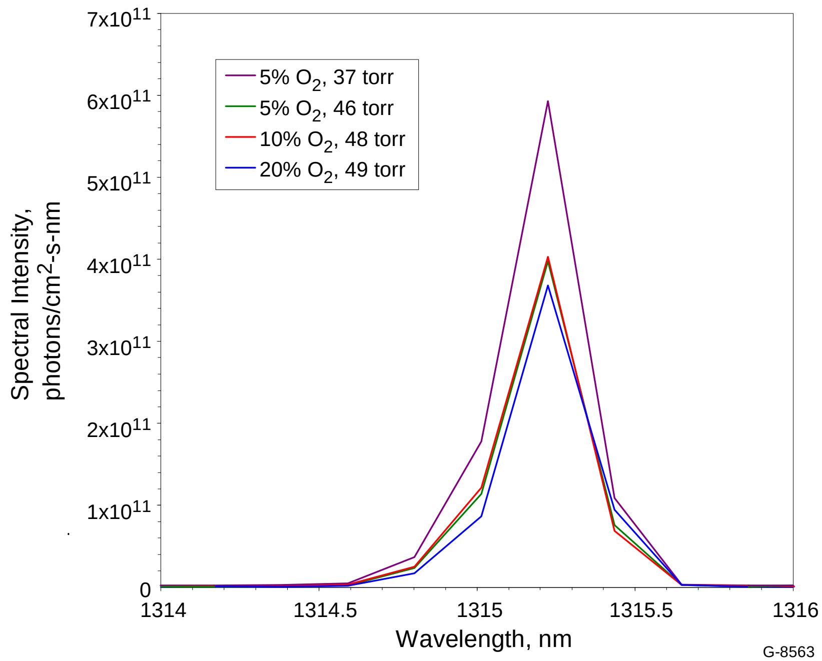
- **InGaAs array – monochromator: observe entire band**
- **Concentration = Intensity ÷ Einstein coefficient**

$O_2(a^1\Delta_g \rightarrow X^3\Sigma_g^-)$



- **A_{00} = 2.20 x 10^{-4} s^{-1} (±10%)**
- **Detection limit ~ 5 x 10^{12} cm^{-3} (5 cm path)**

$I(^2P_{1/2} \rightarrow {}^2P_{3/2})$



- **A = 8.0 s^{-1} (±20%)**
- **Detection limit ~ 10^8 cm^{-3} (5 cm path)**

NIR Photometric Calibration: $O_2(a)$ and I^* Emission

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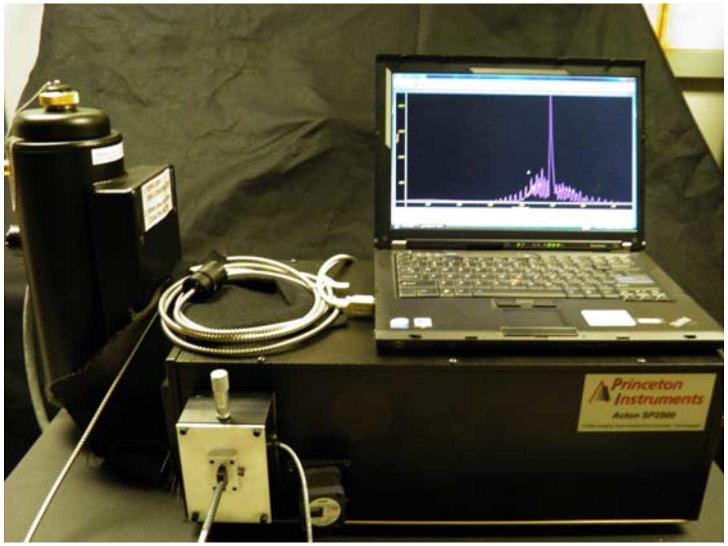

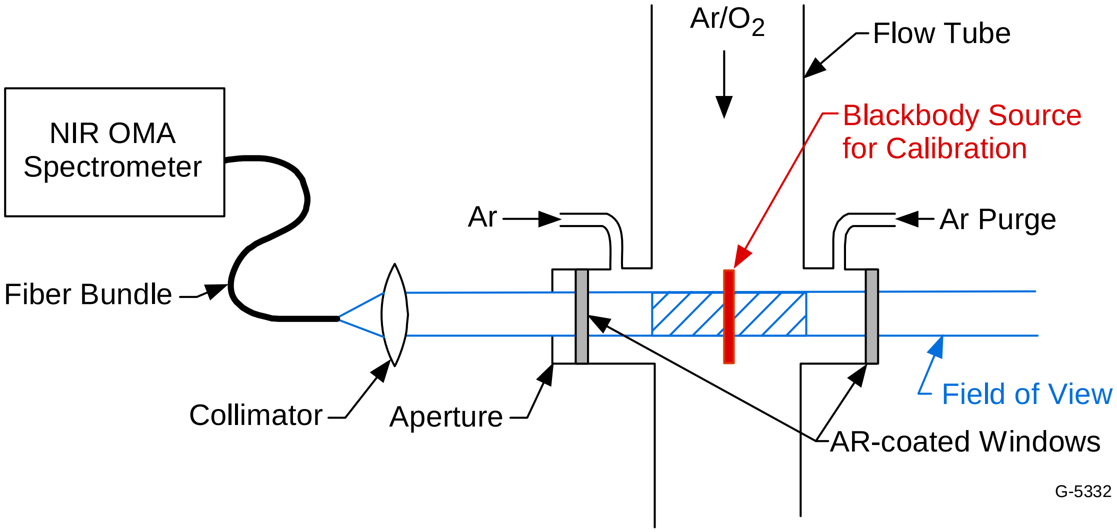

- **Collimated field of view: no reflective surfaces**
  - Eliminate stray light, e.g. discharge emission
- **Etendue (AΩ) for calibration is identical to that for volume emission**
- **Spectral responsivity = (signal) / (Planck function)**
- **Blackbody calibrations 800-1000º C agree within 1%**

Principle of Absolute Calibration Method

- **Instrumental signal for both blackbody and O_2(a→X) emission:**
  - $S(\lambda) = F(\lambda)\ T(\lambda)\ A\Omega\ \delta\lambda\ I(\lambda)$ F = spectral responsivity
  - Use the same $\{A\Omega\ \delta\lambda\}$ for calibration and gas emission measurements
- **Determine F by measuring blackbody spectrum (Planck function):**
  - $F(\lambda) = S_{BB}(\lambda) / N(\lambda, T_{BB})$ $T_{BB} \sim 1000$ C
  - Area of source > area of fov
  - Accuracy <1%
- **Gas radiance in photons/cm²-s-sr-nm:**
  - $I_{aX}(\lambda) = S_{aX}(\lambda) / \{F(\lambda)\ T(\lambda)\}$
  - Correct for spectral baseline/background
- **Determine O_2(a) concentration from spectrally integrated intensity:**
  - $[O_2(a)] = (4\pi/\ell) \int I_{aX}(\lambda) d\lambda / A_{aX}$ A_{aX} = Einstein coefficient

Spectral Fitting Analysis: $[O_2(a,v)]$, T_{rot}

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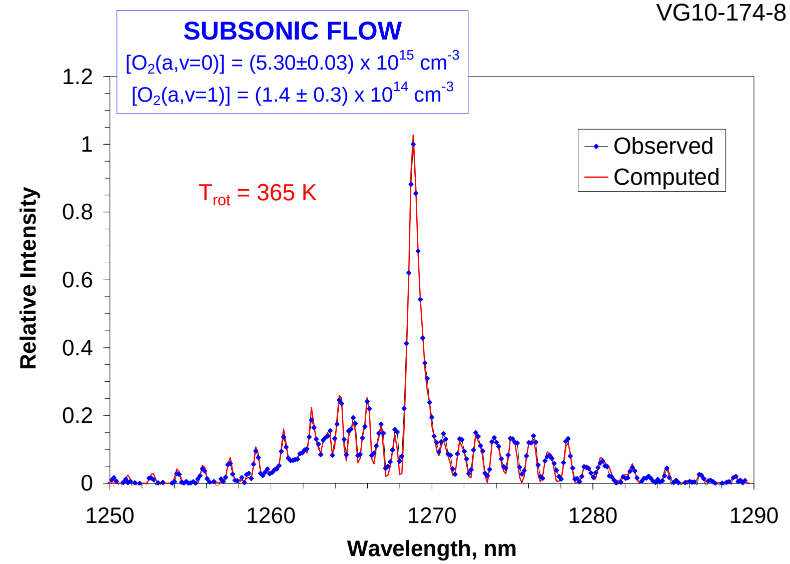
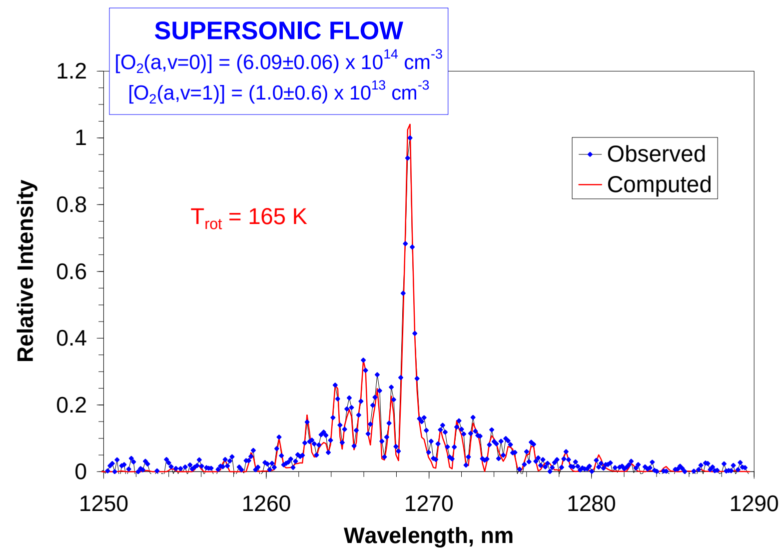
- **$O_2(a^1\Delta_g \rightarrow X^3\Sigma_g^-)$ spectroscopy:**
  - Magnetic dipole transition
  - Hund's coupling case (b)
  - Bose-Einstein statistics ($^{16}O_2$)
  - ➔ 9 rotational branches

- **Our procedure: determine line strengths for (0,0) from line-by-line compilation (HITRAN)**
  - Boltzmann rotational temperature
  - Shift (0,0) envelope to band centers for (1,1), (2,2), etc.

- **Convolve with instrument scan function**
  - Triangular slit function for grating monochromator (0.3 nm FWHM)

- **Linear least squares solutions are $\{[O_2(a,v]\}$**





Estimation of A_{11}, A_{22}, A_{33} Values

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- **Scale values from A_{00} via Franck-Condon factors, transition moment vs. r-centroid:**

  $$A_{v'v''} = (64\pi^4/3h)\,(\nu^3 q_{v'v''})\,(R(r))^2$$

- **Franck-Condon factors, r-centroid values from Krupenie (1972)**

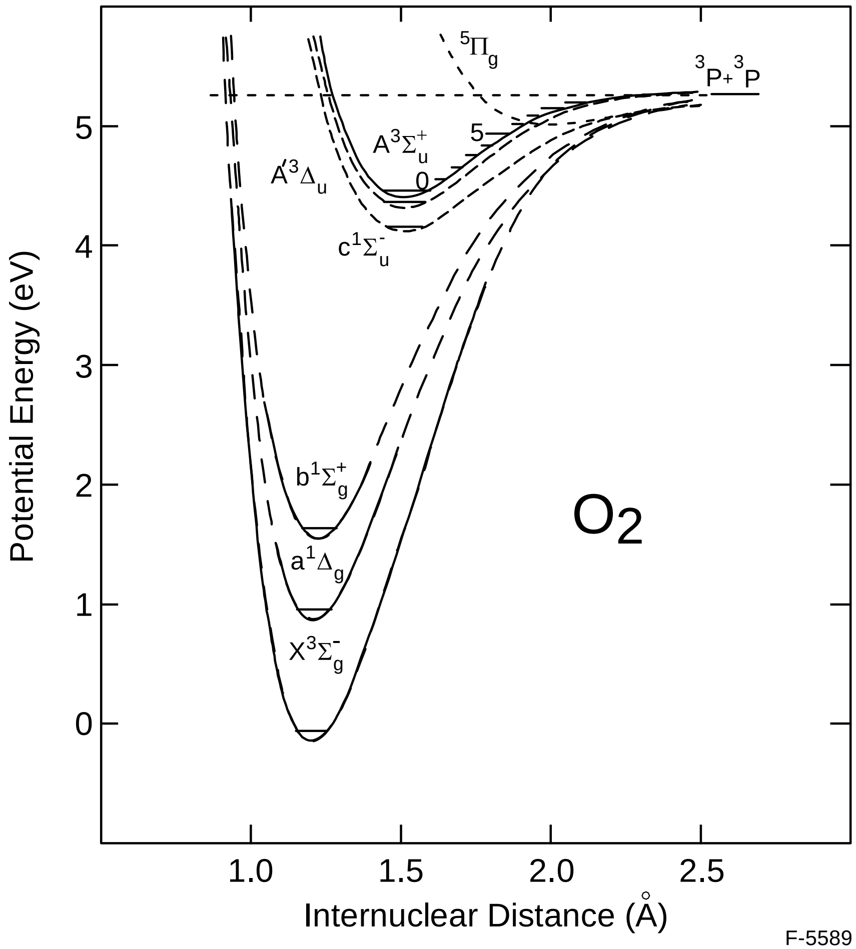
- **Estimate scaling of $(R(r))^2$ from A_{00}:A_{01}:A_{10}**
  - Literature: A_{00}/A_{01} is either ~50 or ~80
  - **PSI measurement: $A_{00}/A_{01} = 52 \pm 6$**
  - Badger et al. (1965): $A_{00}/A_{10} > 200$
  - Solution: $(R(r))^2$ varies slightly with v'

- **Solutions for $A_{00} = 2.20 \times 10^{-4}\ s^{-1}$:**

  $A_{11} = 2.17 \times 10^{-4}\ s^{-1}$

  $A_{22} = 2.12 \times 10^{-4}\ s^{-1}$

  $A_{33} = 2.06 \times 10^{-4}\ s^{-1}$



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BUT WE DO NOT OBSERVE $O_2(a,v>0)$!

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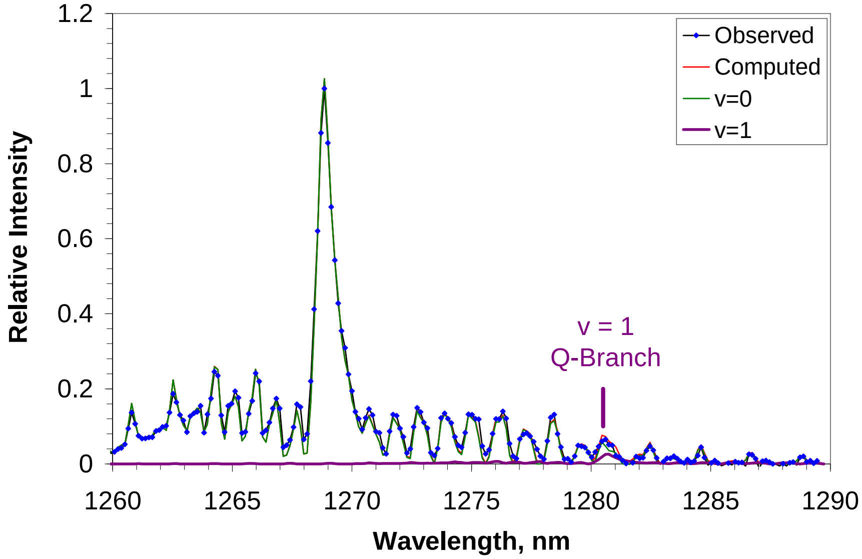

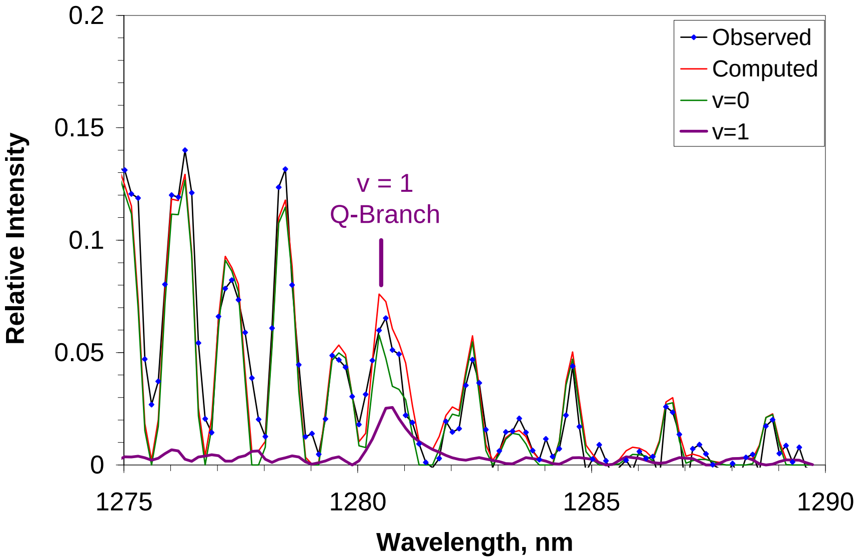

- **Typical fits: [(v=1)]/[(v=0)] ~ 3 to 7 %**
  - Tends to track with temperature of discharge, i.e. thermal populations only
- **True for large range of conditions:**
  - 50 W – 2 kW discharges
  - 0.5 – 50 Torr
  - Cl_2/BHP generators, energy pooling conditions
- **Slanger, Copeland 2003: $O_2(a,v)$ exchange with $O_2(X, v=0)$ is fast**
- **Implications for COIL I_2 dissociation mechanism?**

Spectral Fitting vs. Integration

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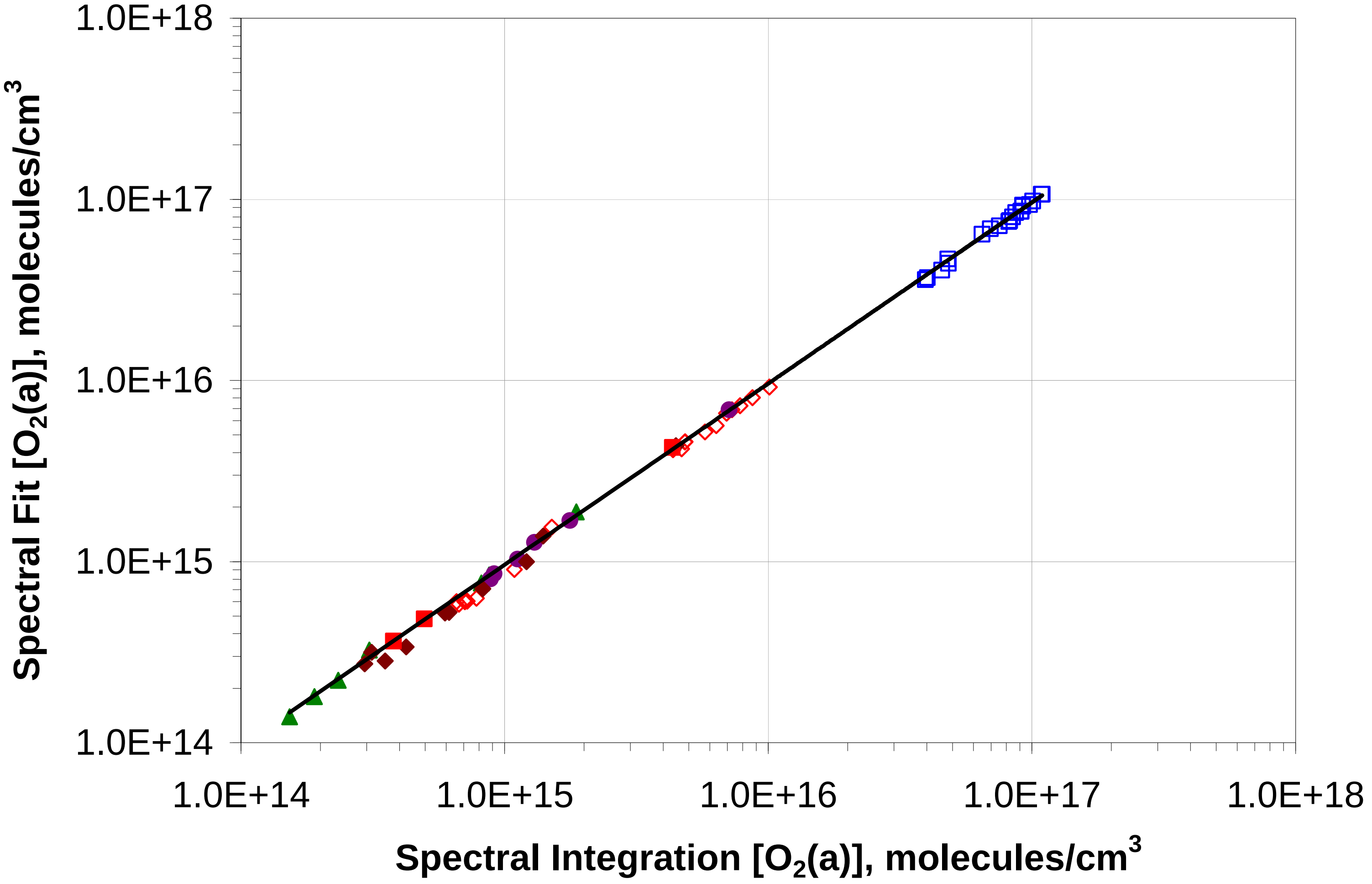

- **Philosophy: spectral fitting confirms band shape, T_{rot}, T_{vib}, no other radiators; then integration gives accurate values**

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Air Afterglow: O + NO → $NO_2 + h\nu$

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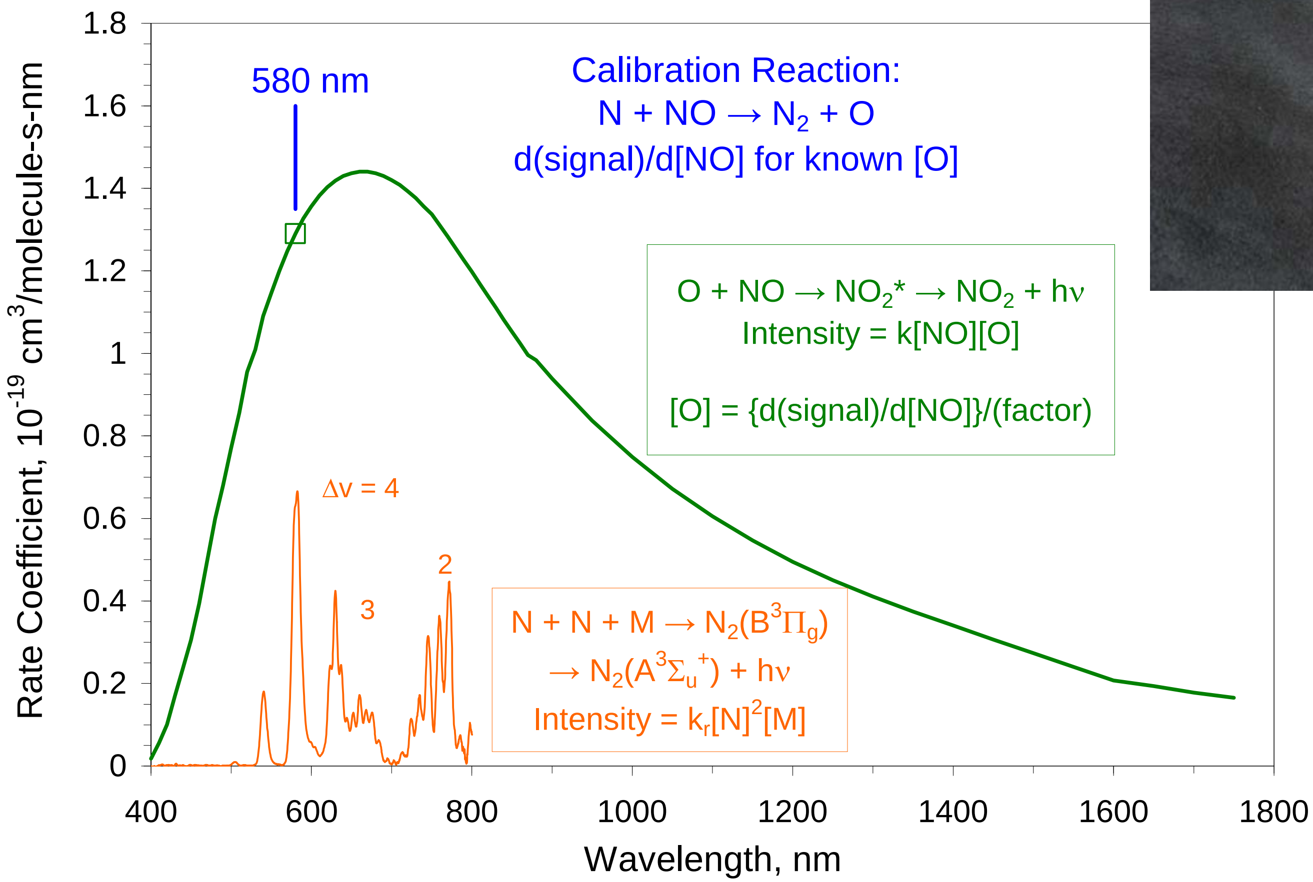
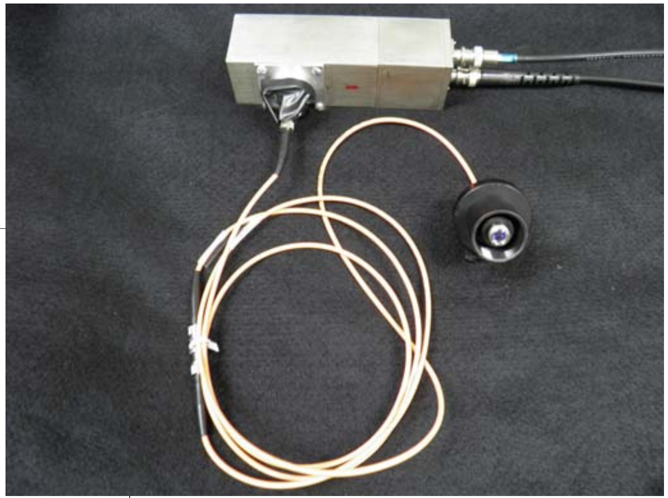
- **Fiber-coupled photomultiplier**
  -- 580 nm filter, collimated field-of-view
- **Calibrate with blackbody <u>and</u> titration reaction**



J. Phys. Chem. <u>90</u>, 320-325 (1986)



- **Calibrations allow measurement of absolute emission rates for known [O], [NO]**
- **→ Determination of k(580 nm)**
- **Scale to other wavelengths via relative intensity measurements**

Air Afterglow: Determination of [O]

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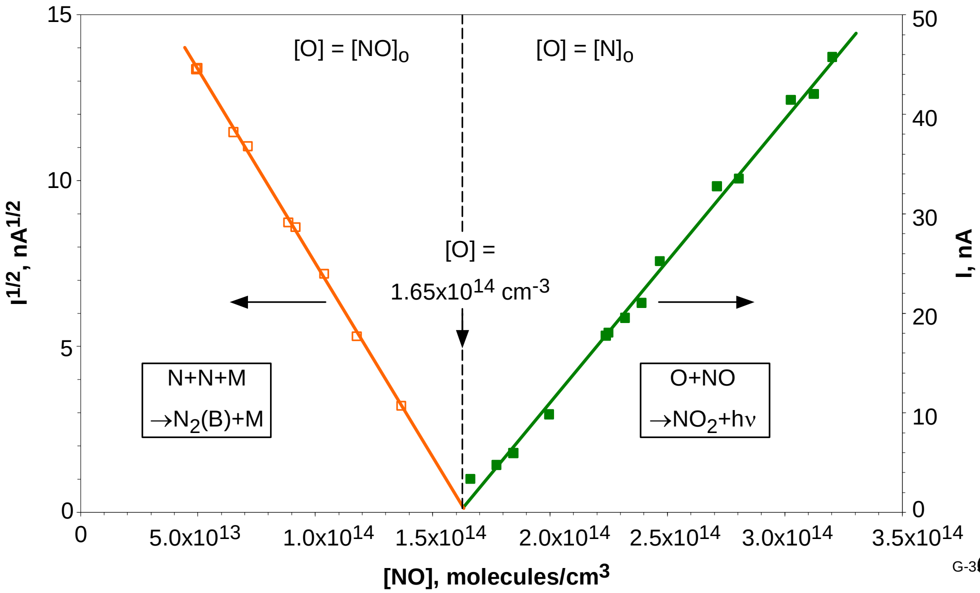

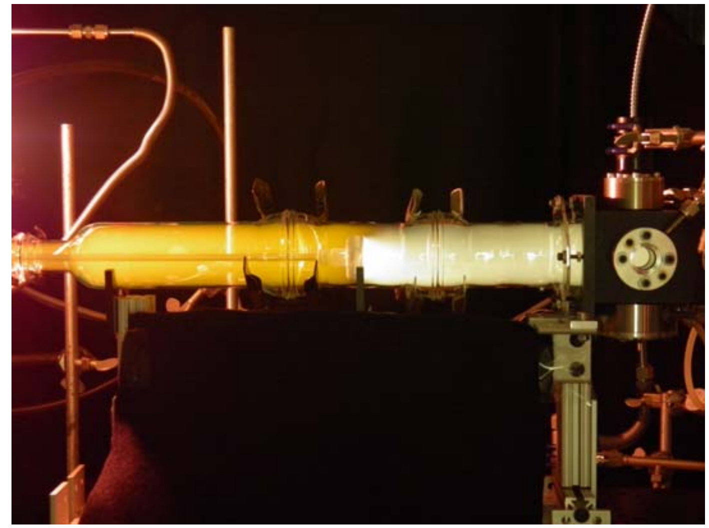

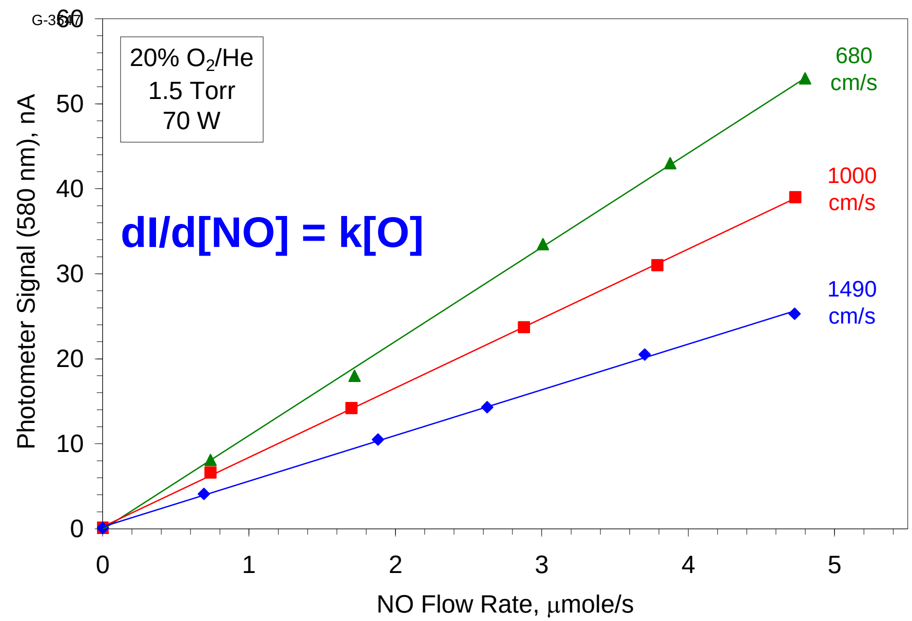

N_2 Discharge: N + NO → N_2 + O

O + NO → NO_2 + hν

For [NO] < [N]: N_2(B→A) emission

For [NO] > [N]: O + NO emission

slope ÷ [O] = calibration factor

correct for O+NO+M reaction

Blackbody calibration: → k_{580}

Measurements: Discharge Production of O, $O_2(a)$

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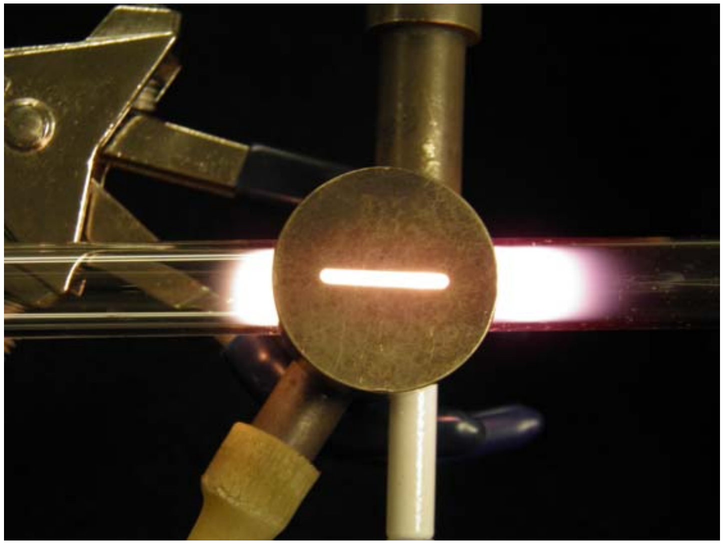

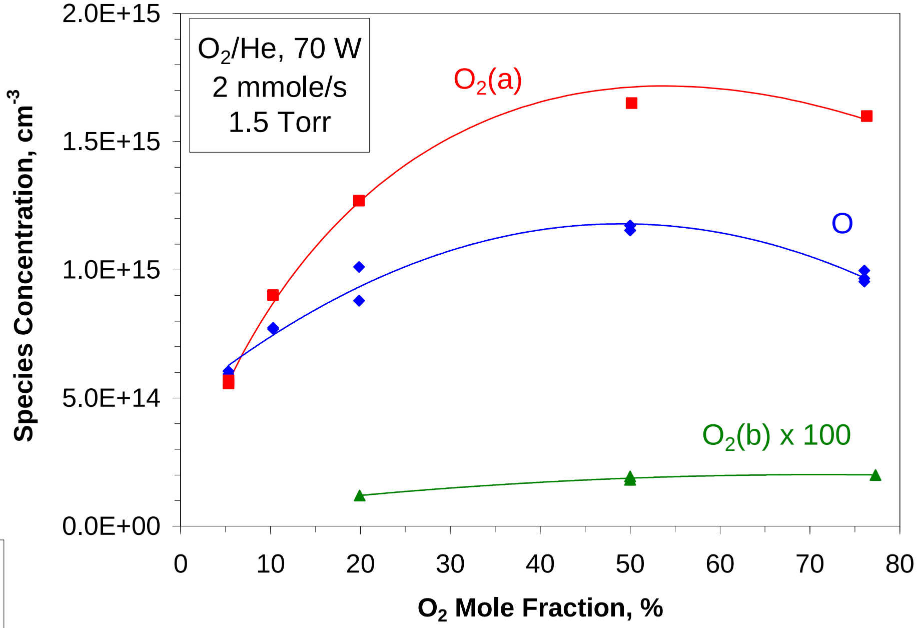

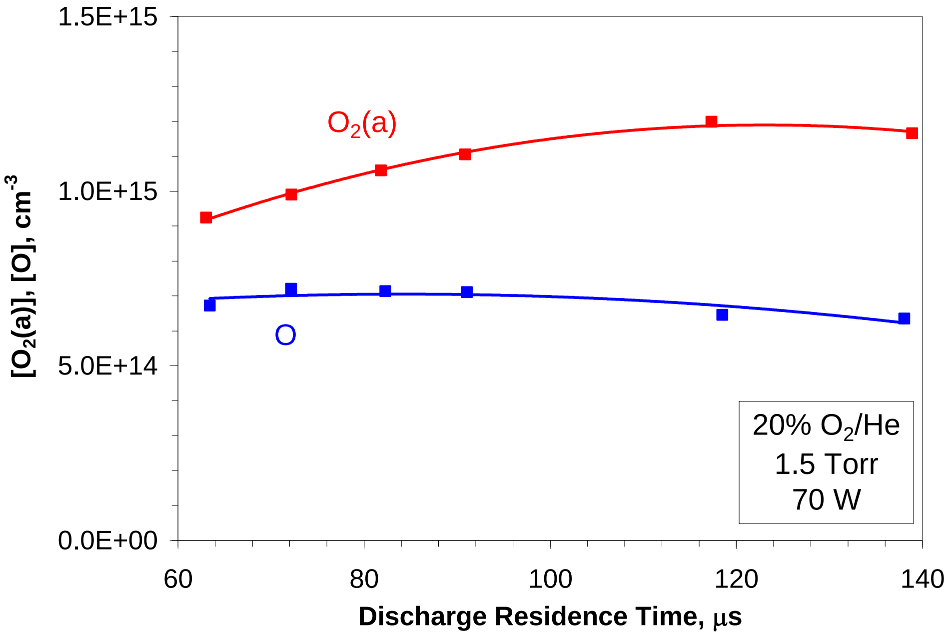

- **Observed $[O]/[O_2(a)]$ is ~ 1 or less**
- **Discharge models predict $[O] >> [O_2(a)]$**
  - **Electron-impact O_2 dissociation cross sections are too large**
  - **Possible O loss on hot walls**

Ultrasensitive Dual-Beam Absorption: O_3 and I_2

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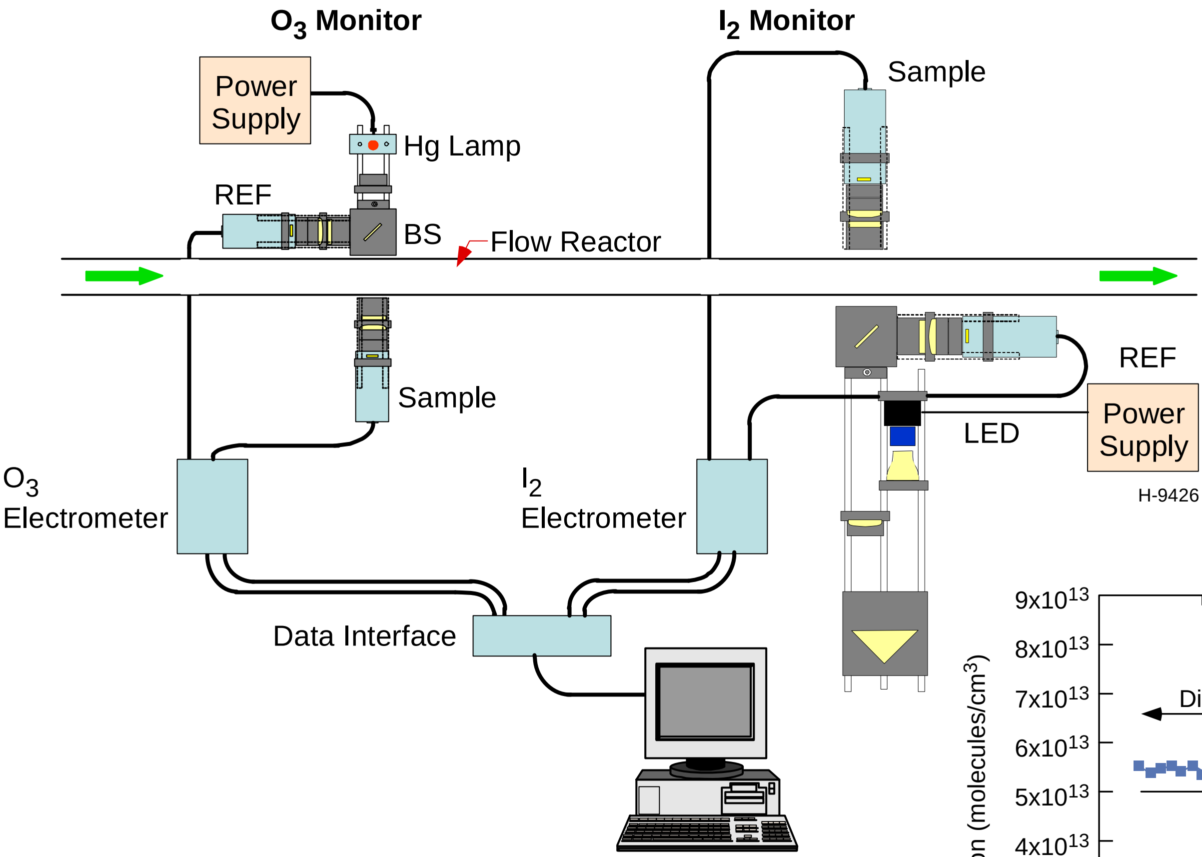
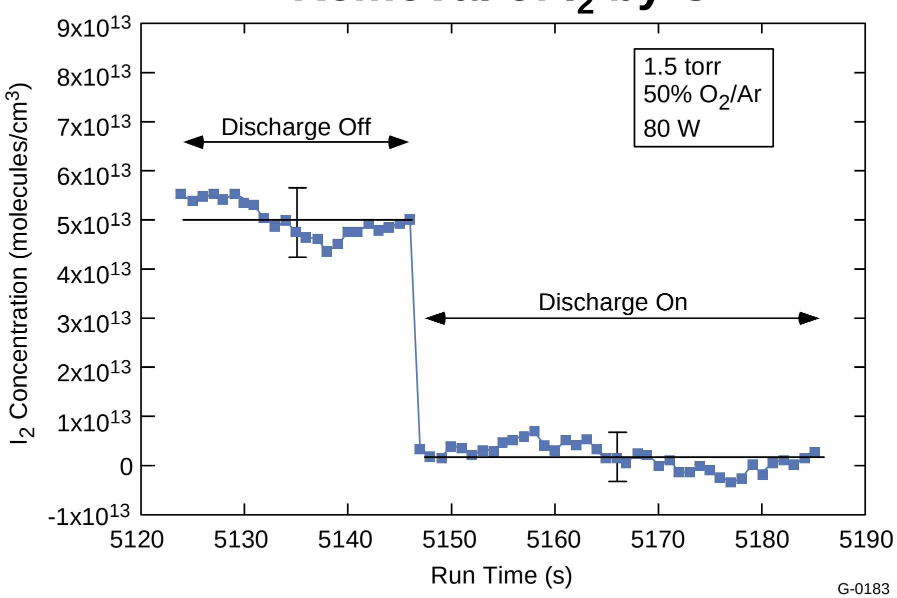


Absorbance = $\ln(I_o/I) = \sigma N \ell$

Detection limit ~ 10^{-5}

Removal of I_2 by O



$\sigma(I_2)$ = 1.64 x 10^{-18} cm^2, 488 nm

$\sigma(O_3)$ = 1.14 x 10^{-17} cm^2, 254 nm

O_3 Formation in Active-Oxygen Flow

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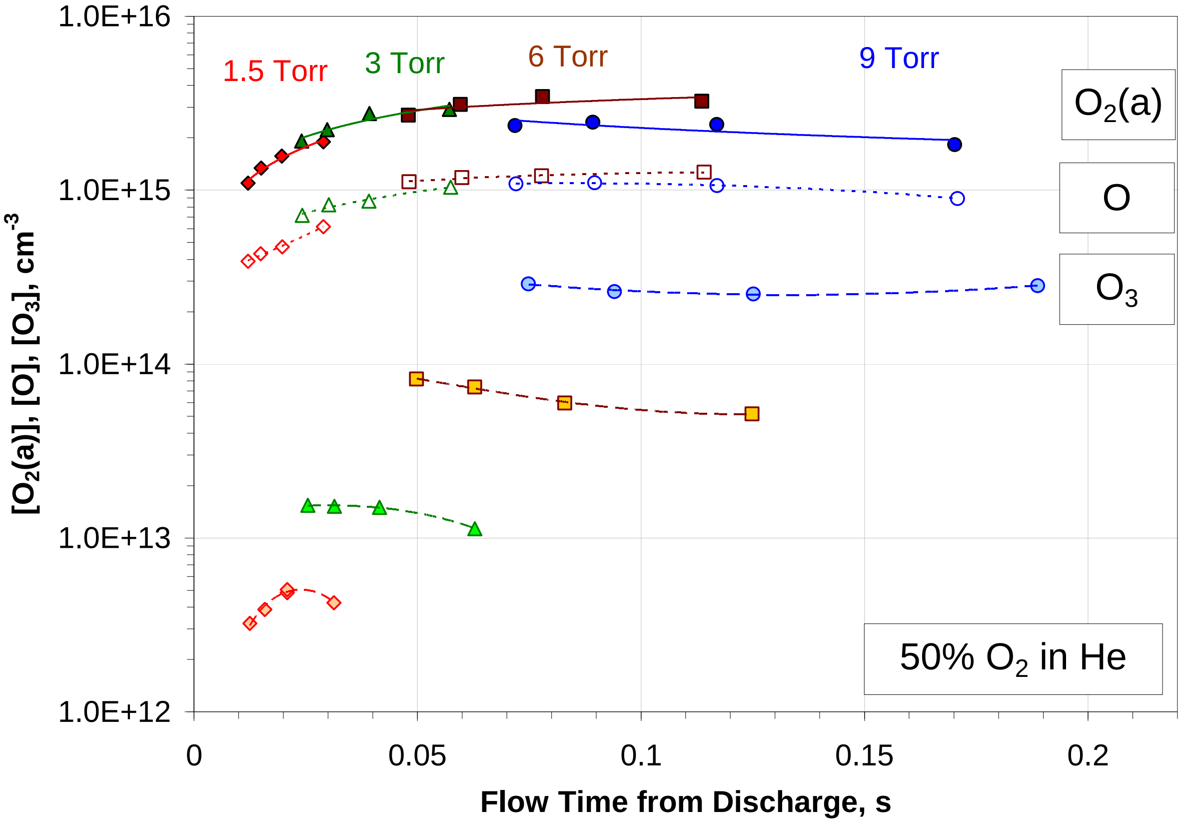

- **Surprise: O and O_3 are in ~ steady state!**
  - **Requires O_3 conversion to O**

$$O + O_2 + M \rightarrow O_3(v) + M$$

$$O_2(a) + O_3(v) \rightarrow O + 2O_2,\ k = 5 \times 10^{-11}\ cm^3/s$$

J. Chem. Phys. 87, 5209-5221 (1987)

Small Signal Gain: Atomic Iodine

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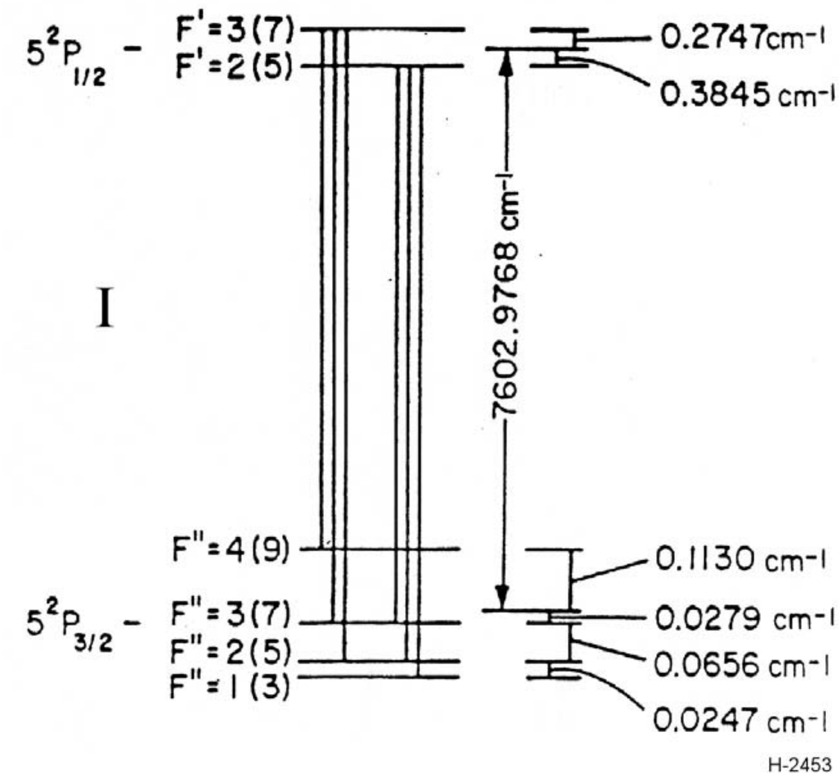
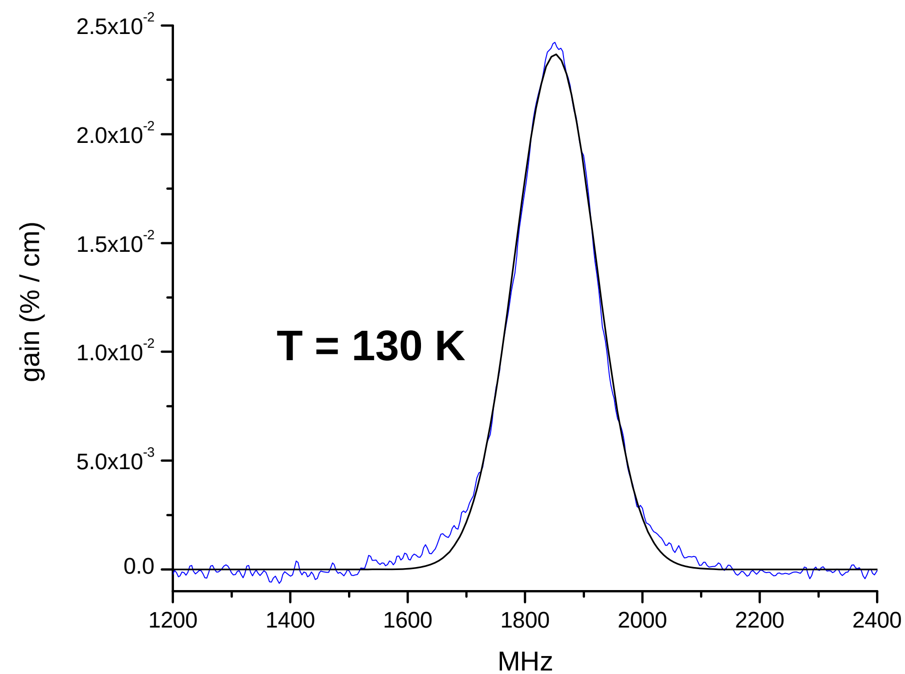


- Probe transmission on (3,4) line
- $G/\sigma(T) = [I^*] – [I]/2$
- $[I^*]$ from IR emission
  → [I], [I*]/[I], ([I*]+[I])/2

- Scanning tunable diode laser
- Balanced ratiometric detection
- Detection limit ~10^{-5} %/cm
- Doppler width → temperature
- Method widely used for COIL, EOIL development



Observations of I*/I Behavior

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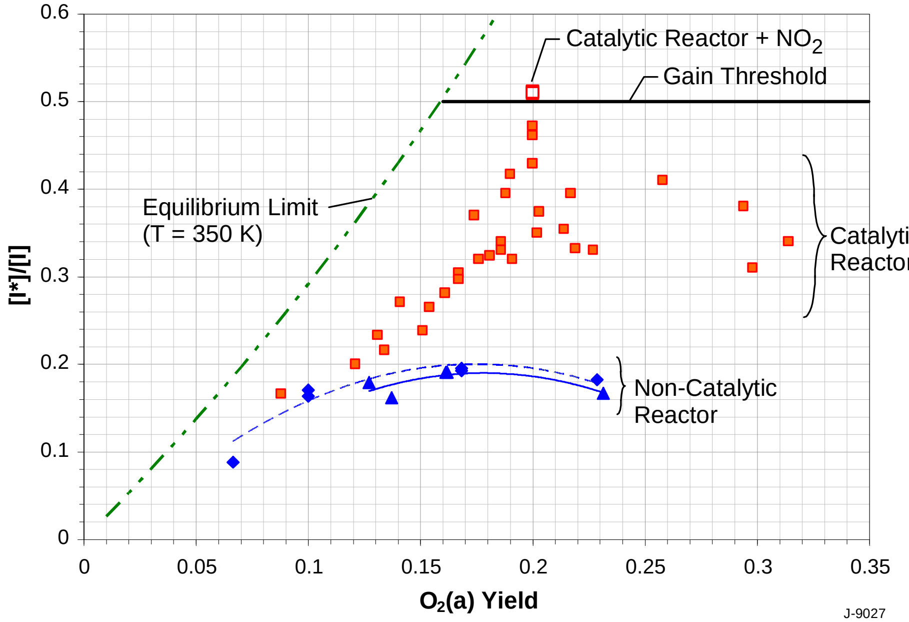
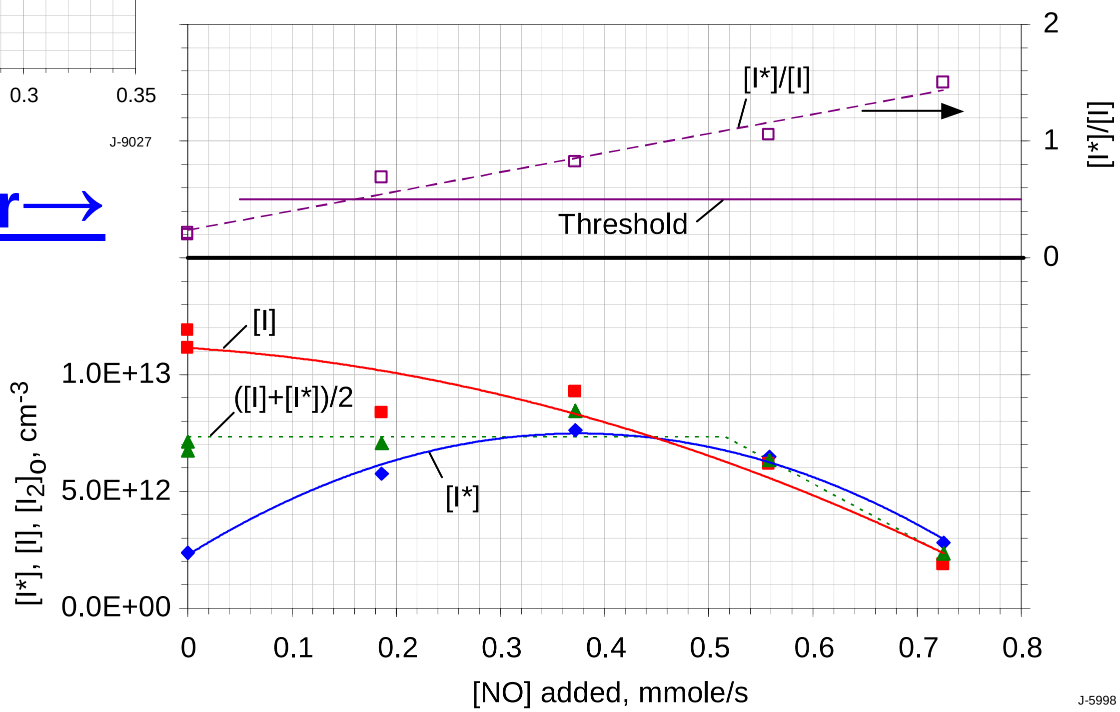


←Subsonic flow reactor

- **I*/I ratio is limited by I* loss reaction**
- **Catalytic environment enhances attainable I*/I**
- **Chem. Phys. Lett. 469, 68-70 (2009)**
  Proc. SPIE 7196-04 (2009)
  Proc. SPIE 7581-06 (2010)

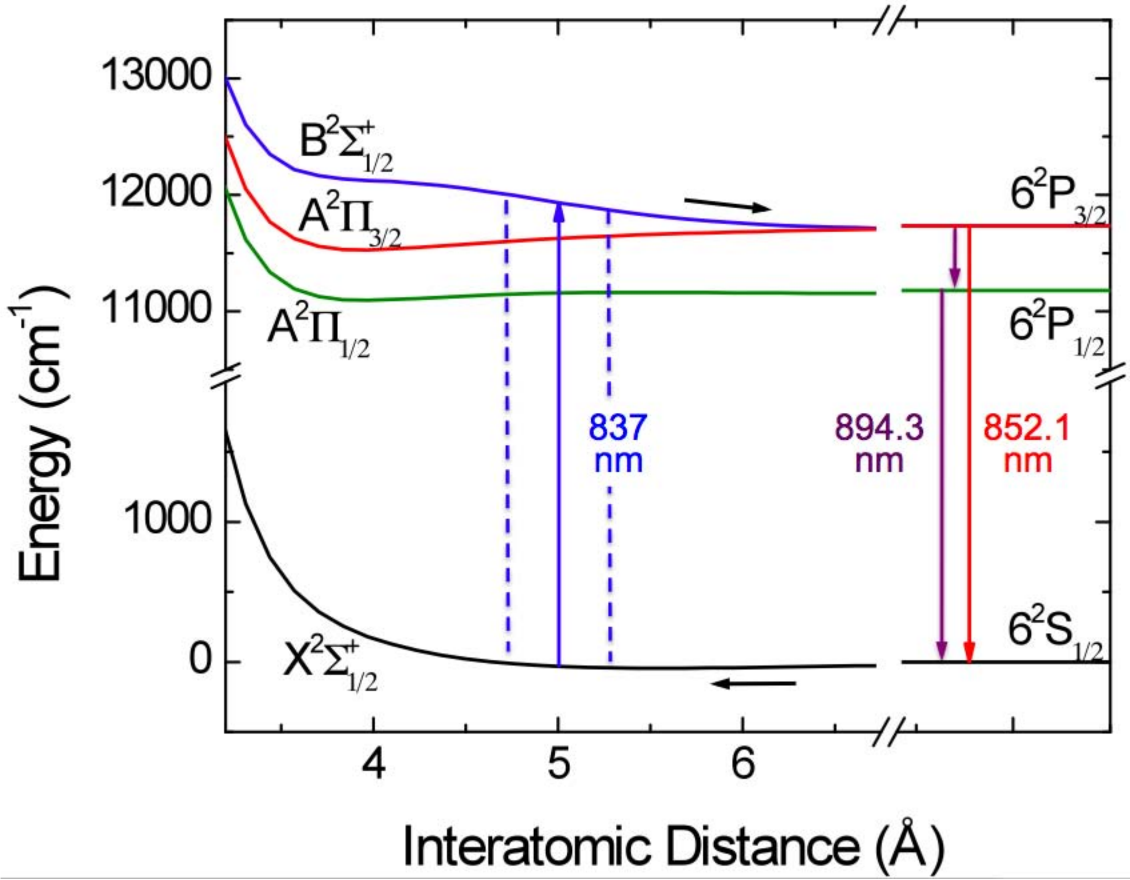
Supersonic flow reactor⟶

- **I*/I ratio is limited by I* loss reaction**
- **Addition of NO enhances I*/I**
- **I*/I continues to increase past optimum gain point**
- **Proc. SPIE 6874-10 (2008)**
  Proc. SPIE 7581-03 (2010)
  J. Appl. Phys. D 43 025208 (2010)



Application to Alkali and Alkali-Exciplex Systems

Cs-Ar Potential Energy Diagram



- **DPAL: pump D_2, lase D_1 (C_2H_6 promotes spin-orbit transfer)**
- **XPAL: pump broadband exciplex X→B, lase on D_1 or D_2**

DPAL/XPAL Gain Measurement Test Bed

(Diode laser scanning D_1 line)

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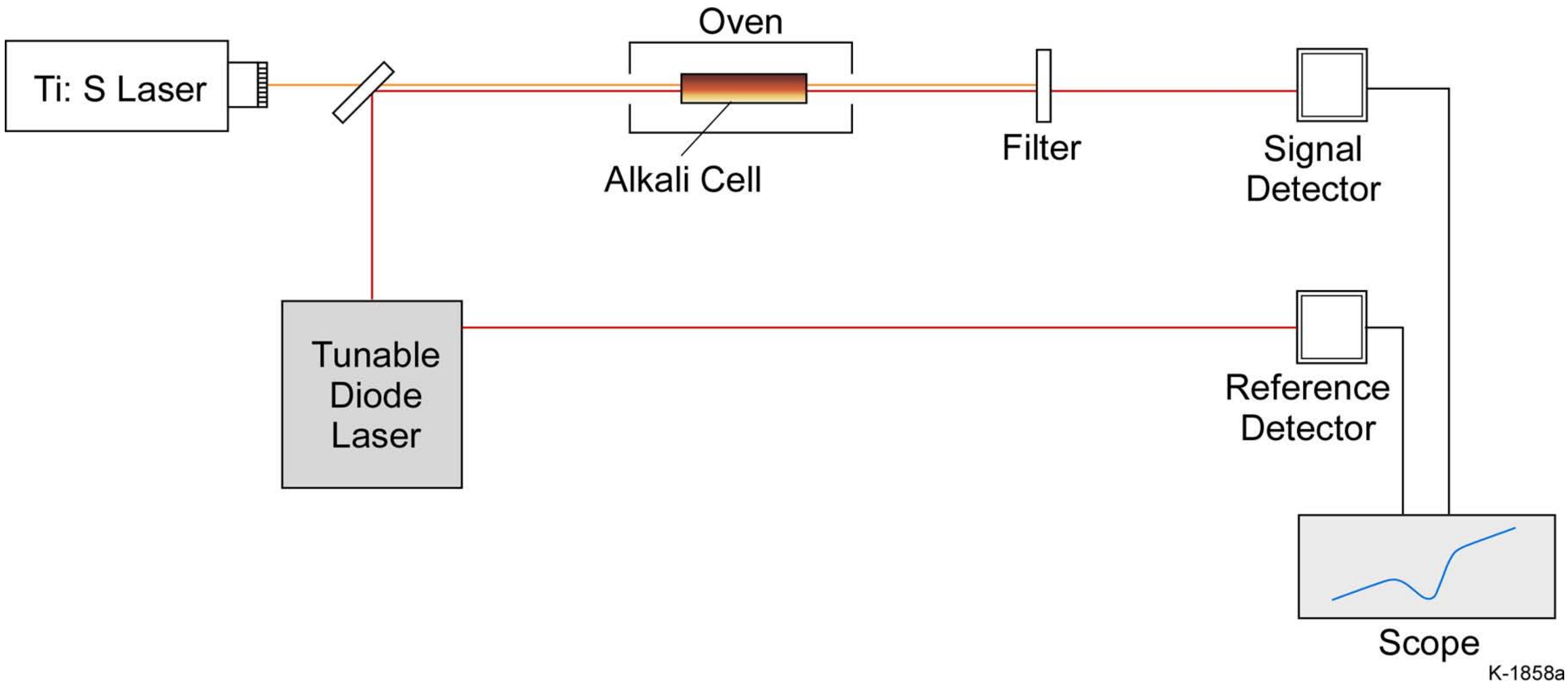

- Direct probe of population inversion dynamics
- Aids in design of optical resonators
- Portable: take to other facilities
- Can extend to spatial imaging of gain
  - Expect significant spatial effects in power scaling
  - Valuable tool for scaling DPAL to high powers

Optical Layout for DPAL/XPAL Gain Measurements

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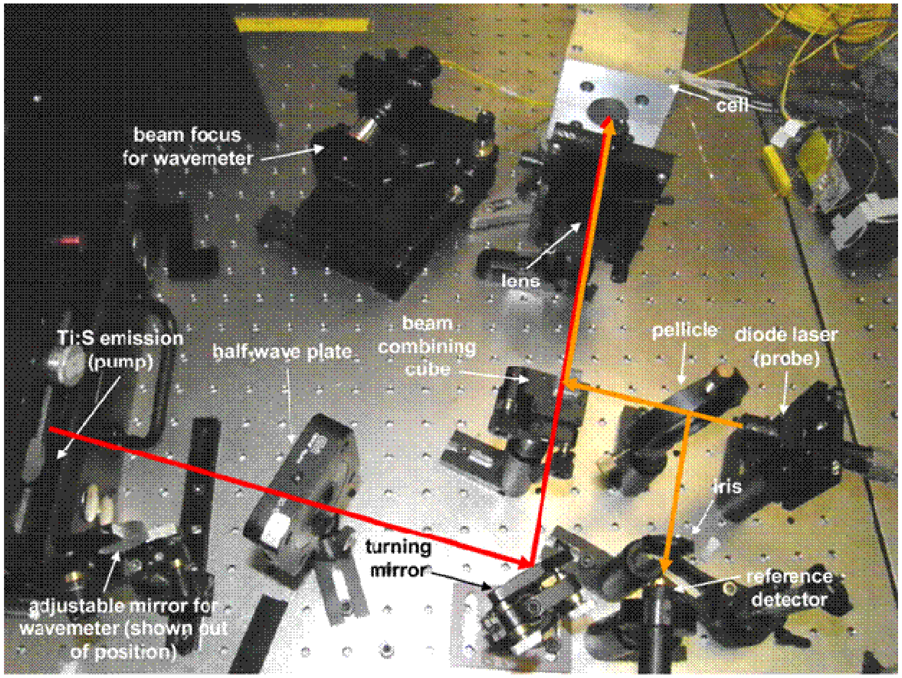

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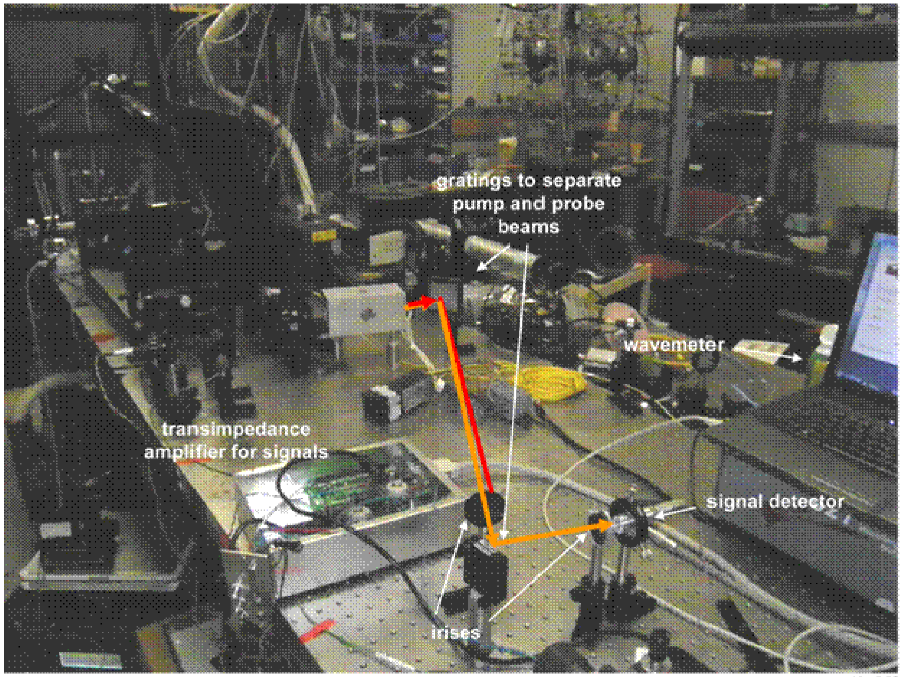

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Computed D_1 Absorption Spectra: Cs

Collisional Broadening Effect

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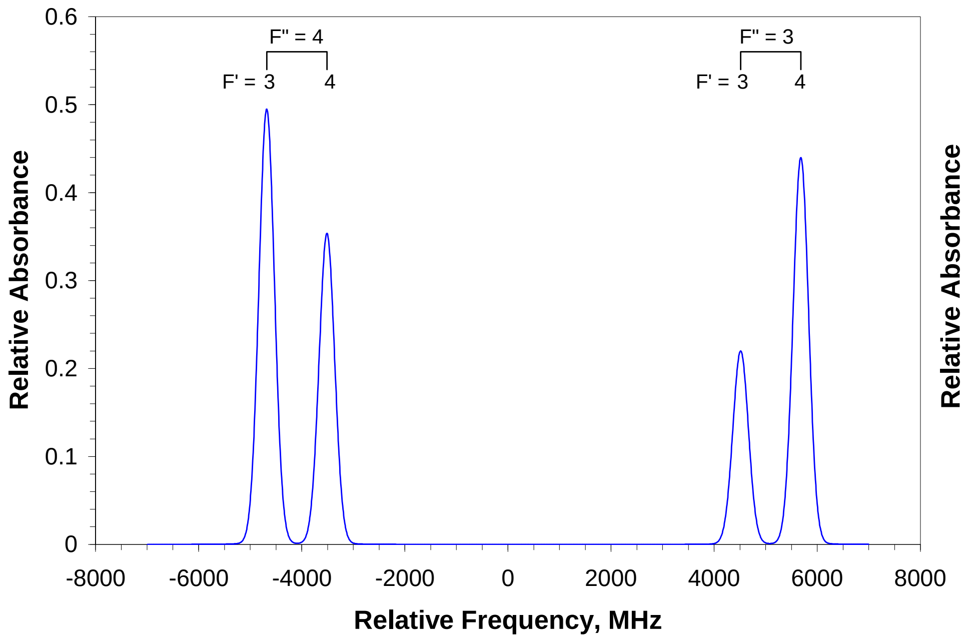
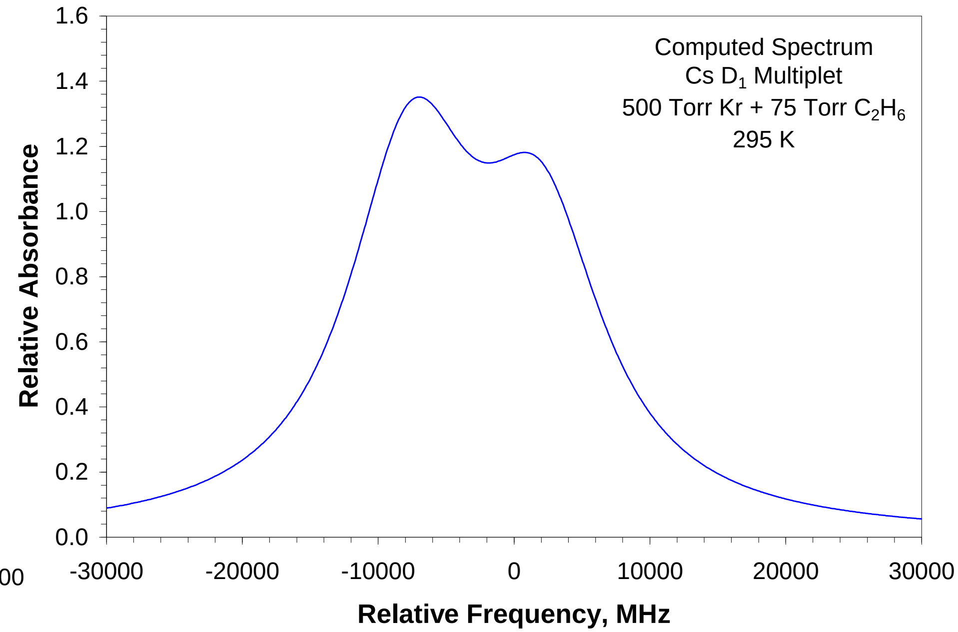
Cs $^2S_{1/2}$ – $^2P_{1/2}$, 894 nm

Low Pressure, Doppler broadening



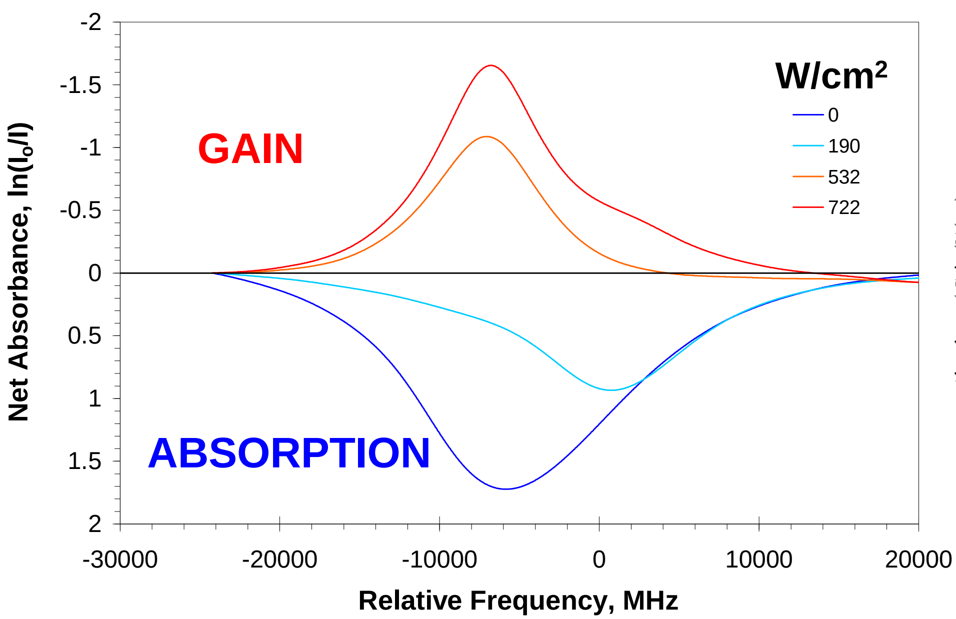
High Pressure, collisional broadening

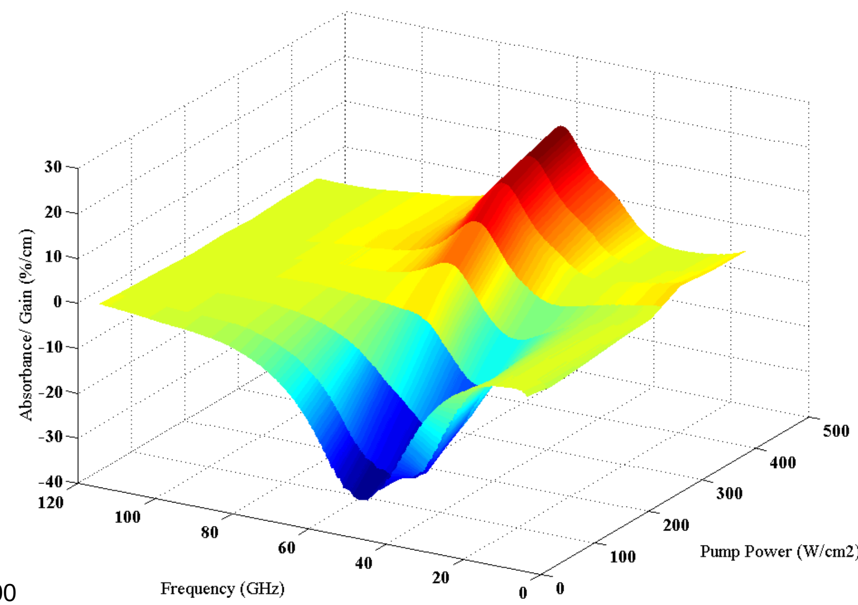


- **Collisional broadening greatly expands required scan range**
- **High optical thickness at elevated temperatures**

Absorption/Gain Spectra: Cs($^2S_{1/2}$,F”=4→$^2P_{1/2}$,F’), 894 nm
500 Torr Kr + 75 Torr C_2H_6, 338 K

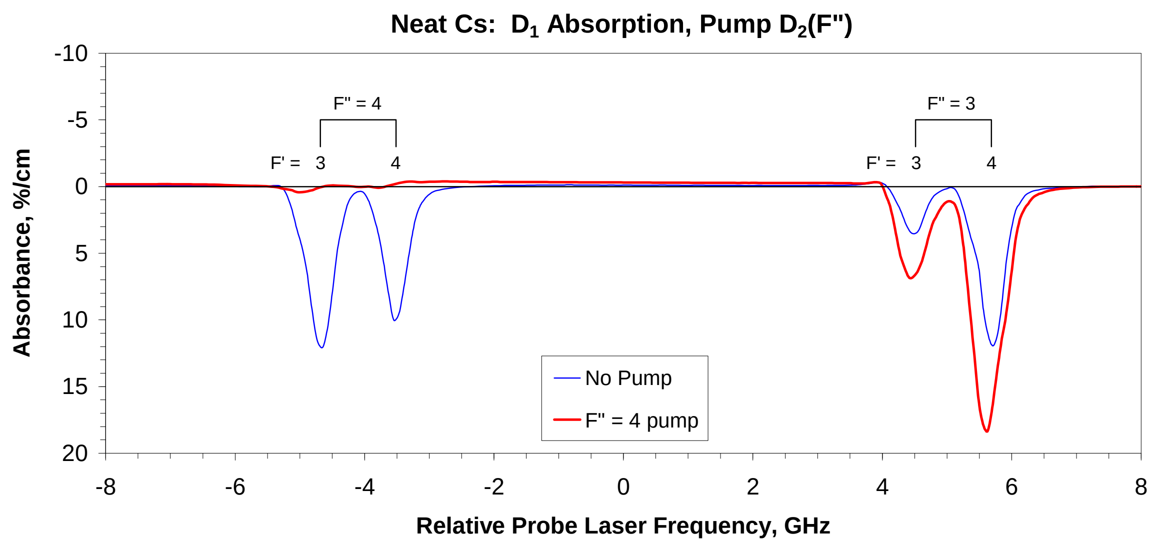
Pump Laser: $^2S_{1/2}$→$^2P_{3/2}$, 852 nm

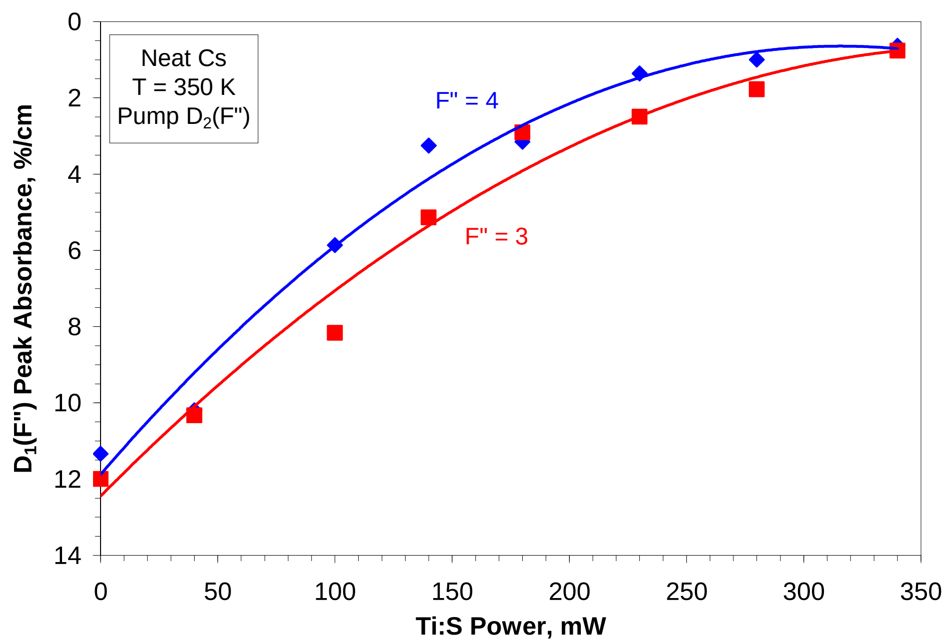




- **Continuing work: investigate absorption and gain dynamics for DPAL, XPAL configurations: Cs, Rb, K**

State-Selected Absorption and Saturation





3-D Image of D_1 Gain, Absorption
Cs + 500 Torr Kr + 75 Torr C_2H_6

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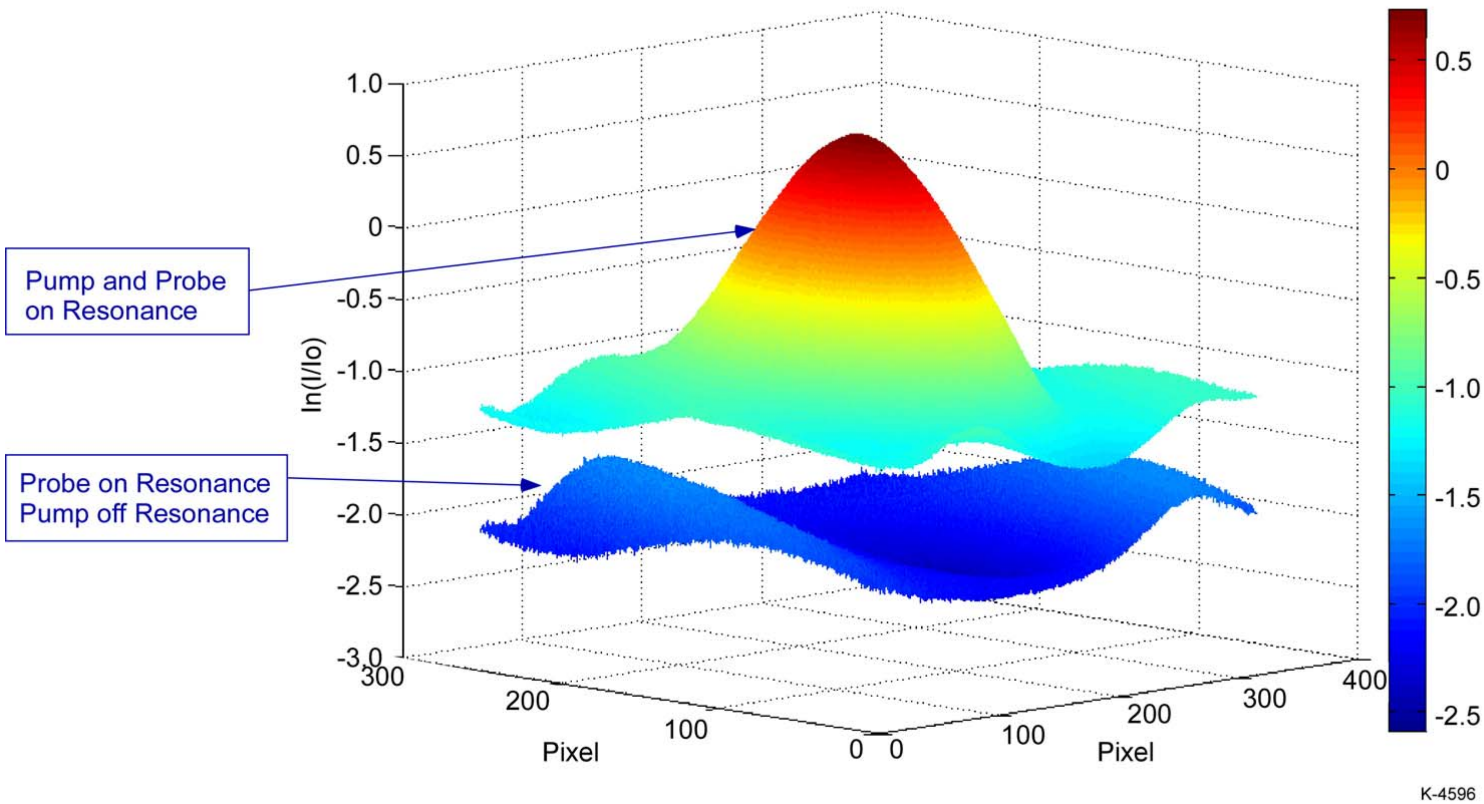
- **Probe beam diameter > pump beam diameter**
- **Sample 9 combinations: probe{on peak, off peak, blocked} x pump{on peak, off peak, blocked}**



- **Gain profile follows Gaussian profile of pump beam**

Conclusions

- **Multispecies diagnostic suite**
  - Absolute emission spectrometry
  - Ultrasensitive absorption photometry
  - Scanning TDL absorption/gain spectroscopy
- **Extreme sensitivity enables subscale operation at low species concentrations**
  - Simplify chemistry, focus on primary reaction steps
  - Transfer to large scale systems: establish models for scaling
- **EOIL, catalytic EOIL, COIL, micro-COIL: operational parametrics**
  - O_2(a) yield vs. small-signal gain
  - I_2 dissociation: [I_2], [I*] + [I]
  - O, O_3 effects
- **DPAL, XPAL: power scaling phenomena**
  - Gain vs. pump power, spatial effects at high optical depth
  - General emission spectroscopy: multi-photon effects vs. pump power

Acknowledgements

Air Force Office of Scientific Research
High Energy Laser Joint Technology Office
Air Force Research Laboratory
Defense Advanced Research Projects Agency

PSI

Daniel Maser
David Oakes
Lawrence Piper

MIT

Carol Livermore

UIUC/CUA

David Carroll
Wayne Solomon
Joe Verdeyen
Gary Eden
Joe Zimmerman
Andrew Palla
Brian Woodard
Gabriel Benavides

AFRL

Tim Madden
David Hostutler

Emory University

Michael Heaven